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MORPHOLOGY AND MECHANICAL BEHAVIOR OF ISOMERIC GRAFT COPOLYMERS--ETC(U)
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AFOSR-76-2945

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AFOSR-TR-78-1630

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6 MORPHOLOGY AND MECHANICAL BEHAVIOR OF
ISOMERIC GRAFT COPOLYMERS AND INTERPENETRATING POLYMER NETWORKS

7 FINAL REPORT, 1 oct 75-3p Sep 78

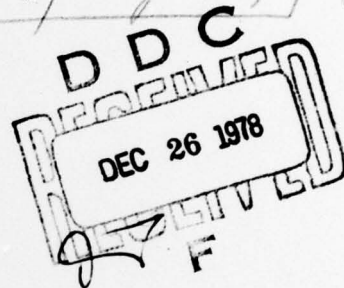
by

10 L. H./Sperling

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October 1, 1975 to September 30, 1978



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Grant No. AFOSR-76-2945

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SUMMARY

This final report describes three years of research under contract AFOSR76-2945 and amendments A and B. The major accomplishments encompass four areas of research:

(1) Controlled grafting of Simultaneous Interpenetrating Polymer Networks. This research, which elucidated the relationship between polymer 1/polymer 2 compatibility and deliberately introduced graft sites, has now been accepted for publication by Polymer Science and Engineering. This portion of the research is summarized in Appendix I. From an engineering point of view, the controlled morphology produced using epoxy/acrylic combinations yielded very tough, novel plastics.

(2) Novel Staining Techniques for Saturated Two-Phased Polymers. Up till now, the only good staining technique for polyblends utilized an osmium tetroxide attack on polymer containing double bonds. The research under this contract showed how this method could be successfully extended to carboxyl or ester containing systems such as acrylics or methacrylics. Now submitted to Polymer Letters, this research is summarized in Appendix II.

Material in Appendices I and II is in press:

- [1] P. R. Scarito and L. H. Sperling, "Effect of Grafting on Phase Volume Fraction, Composition, and Mechanical Behavior: Epoxy/Poly/n-butyl acrylate) Simultaneous Interpenetrating Networks", accepted, Polym. Eng. Sci.
- [2] N. Devia, J. D. Lipko, and L. H. Sperling, "Applications of Kanig's Staining Technique to the Study of Simultaneous Interpenetrating Network Morphology by Transmission Electron Microscopy", submitted to Polymer Letters.

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(3) Polymer Blend and Interpenetrating Polymer Network Nomenclature.

A major stumbling block in the development of multicomponent polymer systems has been an inadequate nomenclature. This research has yielded the following publications:

[3] L. H. Sperling, K. B. Ferguson, J. A. Manson, E. M. Corwin, and D. L. Siegfried, "Isomeric Graft Copolymers and Interpenetrating Polymer Networks. Theory and Experiment.", *Macromolecules* 9, 743 (1976).

[4] L. H. Sperling and E. M. Corwin, "A Proposed Generalized Nomenclature Scheme for Multipolymer and Multimonomer Systems", to appear in "Advances in Chemistry" Series, Issue to be edited by S. L. Cooper.

(Portions of [4] above will be found in Appendix III.)

(4) The first experiments on decrosslinking of interpenetrating polymer networks was done under the auspices of this contract. This work was recently published:

[5] S. Yomoda and L. H. Sperling, "Viscoelastic Behavior of Partly Decrosslinked Polymer Networks. I. Acrylic Acid Anhydride-Crosslinked Poly(ethyl acrylate)", *J. Appl. Polym. Sci.*, 21, 2609 (1977).

This work is summarized in Appendix IV.

Overall, significant progress was achieved in several areas of research. Several papers have either already appeared in print or will do so in the coming months.

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People Involved:

Senior Investigator:

L. H. Sperling

Students and Associates:

S. Yomoda

B. Atlig

N. Devia

P. Scarito

E. Corwin

J. Lipko

Oral Presentation of Works:

- [1] "A Proposed Nomenclature Scheme for Multipolymer Materials", Akron Polymer Lecture Group, March, 1978.
- [2] "Isomeric Graft Copolymers and Interpenetrating Polymer Networks", ACS Meeting, Anaheim, March, 1978.
- [3] "Decrosslinking of IPN's", ACS Meeting, New Orleans, March, 1977.
- [4] "Interpenetrating Polymer Networks and Related Materials", Stauffer Chemical Co., November, 1977.
- [5] "Electron Microscope Studies of Polymer Blends, Blocks, and IPN's", Ethicon, January 1978.

APPENDIX I

Grafted simultaneous interpenetrating polymer networks (SIN's) were prepared from Epon 828 epoxy resin and n-butyl acrylate monomer. The amount of grafting monomer (glycidyl methacrylate) was found to affect profound changes in the morphology and mechanical behavior of these materials. While the size of the dispersed rubbery phase increased from approximately 2 microns to 20 microns, the number of domains decreased, with increasing amounts of grafting agent. The total dispersed phase volume decreased with increased grafting. At the highest level of grafting, the two-phase morphology disappeared and only one phase was observed. With increased grafting, dynamic mechanical spectroscopy showed a movement of the loss modulus peaks toward each other, confirming an increase in compatibility in the system and showing that the compositions in each phase were becoming more alike. The SIN with the most glycidyl methacrylate (3.0%) showed only one peak in the loss modulus curve, supporting the single phase morphology found through microscopy.

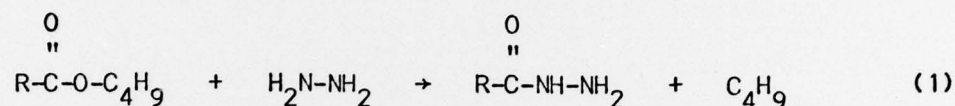
At the point of compatibility between the two networks, the SIN supermolecular structure may be visualized as becoming one complex network, where the number of grafts between the two polymer chains outnumbers the number of homopolymer crosslinks. The chemical grafts were also shown to significantly alter the free energy of mixing of the two polymers. A grafting level-composition phase diagram showed that at well defined levels of grafting the free energy of mixing goes from a positive value to a negative value.

APPENDIX II

Morphological characterization constitutes an important step required in understanding the effect of synthesis conditions on the final properties of polymer blends. While a few polymer mixtures are known to form homogeneous solid solutions, most multi-polymer combinations are chemically incompatible and some degree of phase separation occurs. It is recognized that changes in morphological details such as degree of phase continuity, phase composition, domain size, and phase structure induce significant changes in physical and mechanical properties.

Transmission electron microscopy (TEM) stands out among all of the methods employed for studying morphology because its higher resolution power allows the direct observation of submicroscopic structures. To date, the most successful method for studying the morphology of polymer blends containing an unsaturated polymer has been the osmium tetroxide (OsO_4) staining technique developed by Kato. The procedure involves the reaction of the OsO_4 molecule across points of unsaturation in a polymeric component, usually a diene-based elastomer. This reaction has the dual effect of hardening the rubber so that it is easier to section and selectively fixing the osmium atom in just one polymer. Due to the higher electron density of the osmium atom, the electron beam is scattered, providing contrast with the saturated polymer. The method has been a powerful tool in revealing the morphological features of many saturated-unsaturated polymer combinations, but its applicability to saturated polymers has been rather limited. Alternative techniques have involved the incorporation of small quantities of diene compounds during synthesis, the use of iodine, and other heavy elements. Although reasonable success with some saturated polymers can be obtained, no general method has been available.

Kanig (8) recently reported a new staining technique which allows contrast in blends containing esters or carboxyl groups, such as acrylics. The acrylate polymer is first treated with hydrazine or hydroxylamine, followed by osmium tetroxide staining in the absence of water. The first reaction involves the formation of a hydrazide according to



Staining is obtained by deposition of metallic osmium through the reducing action of the hydrazide.

This communication relates to the application of Kanig's technique (8) to epoxy/poly(n-butyl acrylate) simultaneous interpenetrating networks (SIN's), using samples that were previously characterized by scanning electron microscopy (SEM)(9).

Synthesis

Epoxy/poly(n-butyl acrylate) SIN's previously prepared and studied in this laboratory were used in this work (9). Briefly, SIN's consisted of mixes of 80% Epon 828 resin and 20% n-butyl acrylate. The epoxy was cross-linked by the addition of phthalic acid anhydride while 0.4% diethylene glycol dimethacrylate was used as a crosslinker for the n-butyl acrylate phase. Deliberate grafting between the two networks was introduced by addition of 0 to 3% glycidyl methacrylate.

APPENDIX III

The number of two-polymer, multipolymer and multimonomer systems reported in the scientific and patent literature continues to rise, without an adequate nomenclature to describe the several materials. In addition to the usual required molecular specifications, the time sequence of synthesis in grafting, crosslinking, and polymerization is important in many cases and needs to be preserved in any nomenclature system for a full definition of the final product.

This paper is divided into three parts:

(1) A proposed nomenclature system, which employs a short list of elements (polymers or polymer reaction products). These elements are reacted together in specific ways by binary operations which join the two polymers to form blends, grafts, blocks, crosslinked systems or more complex combinations.

(2) The relationship between the proposed nomenclature and the mathematics of ring theory (a form of the "new math") is discussed. It is shown that a simplified form of the nomenclature forms a series of related mathematical rings.

(3) Since the new nomenclature and its mathematical background yield insight into the actual synthetic schemes and their interrelationships, novel structures and compositions are suggested. A few experimental examples new in the literature are mentioned to show how the new nomenclature scheme has already been employed to discover new multipolymer systems.

APPENDIX IV

Acrylic acid anhydride (AAA) and tetraethylene glycol dimethacrylate (TEGDM) were employed as labile and permanent crosslinking monomers for poly(ethyl acrylate), respectively. Upon partial or total hydrolysis of the AAA crosslinks, various states of viscoelastic creep and stress relaxation were brought about. The use of chemically active monomers for crosslinking permits new polymer structures to be synthesized. In this case, decrosslinking converts a thermoset polymer into its thermoplastic counterpart. The relationship between the present decrosslinking study and a new nomenclature theory of grafted and crosslinked polymers is explored.

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| 1. REPORT NUMBER AFOSR-TR- 78-1630 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER | | | | | | | | | | | | |
| 4. TITLE (and Subtitle) MORPHOLOGY AND MECHANICAL BEHAVIOR OF ISOMERIC GRAFT COPOLYMERS AND INTERPENETRATING POLYMER NETWORKS | 5. TYPE OF REPORT & PERIOD COVERED Final Oct 1975-Sept 1978 | | | | | | | | | | | | | |
| | 6. PERFORMING ORG. REPORT NUMBER | | | | | | | | | | | | | |
| 7. AUTHOR(s) L. H. Sperling | 8. CONTRACT OR GRANT NUMBER(s) AFOSR-76-2945 <i>new</i> | | | | | | | | | | | | | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Lehigh University Materials Research Center, Coxe Lab #32 Bethlehem, PA 18015 | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/B2 | | | | | | | | | | | | | |
| 11. CONTROLLING OFFICE NAME AND ADDRESS AF Office of Scientific Research/NC Bolling AFB, D.C. 20332 | 12. REPORT DATE October 1978 | | | | | | | | | | | | | |
| | 13. NUMBER OF PAGES 9 | | | | | | | | | | | | | |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | 15. SECURITY CLASS. (of this report) Unclassified | | | | | | | | | | | | | |
| | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE | | | | | | | | | | | | | |
| 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. | | | | | | | | | | | | | | |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) | | | | | | | | | | | | | | |
| 18. SUPPLEMENTARY NOTES | | | | | | | | | | | | | | |
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20. ABSTRACT


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